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Description

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a flame retarding polyester composition superior in thermal stability, fluidity and mechanical properties.

Description of the Prior Art:

Thermoplastic polyesters such as polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, polycyclohexane dimethylene terephthalate, etc. have found applications in mechanical components, electrical parts, motor vehicle parts and the like. On the other hand, for industrial materials as described above, safety against flames, i.e. flame retardancy, has been strongly required.Besides balancing general chemical and physical properties, with the further requirement that, during injection molding of molded items or heat treatment thereof, the flame retarding agent does not bleed out onto the surfaces of the molded items.

Conventionally, as non-bleed type flame retarding agents for the thermoplastic polyester, there have been proposed polymeric flame retarding agents such as a halogenated polycarbonate (Japanese Laid Open Patent Application Tokkaisho No. 48—52834) and a halogenated epoxy resin (Japanese Patent Publication Tokkosho No. 53—18068), etc. Although the known flame retarding agents as described above, which are mainly composed of tetrabromobisphenol A, are superior in compatibility with respect to polyester, they tend to deteriorate the crystallinity inherent in polyester, thus adversely affecting the mechanical properties, thermal stability, chemical resistance, and electrical properties, etc. of the polyester itself.

Meanwhile, there have also been introduced halogen containing polystyrene and halogen containing poly-α-methylstyrene, together with their applications to thermoplastic polyesters (Plastic Technology, July, 1980, pages 71—74), but in the polyester compounds in which the above flame retarding agents are mixed, marked deterioration of thermal stability and mechanical properties is noticed, with simultaneous reduction of fluidity, thus resulting in poor moldability.

Therefore, it has been desired to realize polyester compounds free from undesirable bleeding out of the flame retarding agent, with simultaneous superior flame retardancy and favorable mechanical properties of polyester itself.

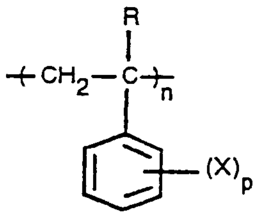
SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a flame retarding polyester compound which is superior in balancing of thermal stability, fluidity and mechanical properties, without bleeding-out of the flame retarding agent.

It has been found that, by employing halogen containing polystyrene and/or halogen containing poly-α-methylstyrene as flame retarding agents, with a further addition thereto of antimony trioxide and epoxy compounds, a flame retarding polyester compound having superior stability and fluidity, and yet favorably maintaining the mechanical properties of polyester itself, can be obtained.

More specifically, the present invention provides a flame retarding polyester composition which comprises

(a) 3 to 45 parts by weight of a halogen containing polystyrene and/or a halogen containing poly-α-methylstyrene represented by formula (I)



(I)

wherein R represents a hydrogen atom or methyl group, X represents a bromine or chlorine atom, p is an integer of 1 to 5, and n is an integer larger than 2,

(b) 1 to 20 parts by weight of antimony trioxide, and

(c) 0,1 to 10 parts by weight of an epoxy compound selected from the group consisting of glycidyl esters of aliphatic or cycloaliphatic carboxylic acids and ethylene-glycidyl methacrylate copolymer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The main component of the thermoplastic polyesters employed in the practice of the present invention are polymers or copolymers prepared by condensing a dicarboxylic acid (or an ester forming compound thereof) with a glycol (or an ester forming compound thereof).

Among the dicarboxylic acids suitable for preparing polyesters in accordance with the present invention are the aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, orthophthalic acid, 2,6-naphthalene dicarboxylic acid, 1,5-naphthalene dicarboxylic acid, bis-(p-carboxyphenyl) methane, 1,2-bis(p-carboxyphenoxy) ethane, anthracene dicarboxylic acid, 4,4′-diphenyl dicarboxylic acid, 4,4′-diphenylether dicarboxylic acid, aliphatic dicarboxylic acids such as adipic acid, sebacic acid, azelaic acid, cycloaliphatic dicarboxylic acids such as 1,3-cyclohexane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid and the like, or ester-forming compounds thereof.

The glycols suitable for preparing polyesters in accordance with the present invention include aliphatic diols having 2 to 10 carbon atoms such as ethylene glycol, 1,3-propylene glycol, 1,4-butanediol, neopentylglycol, 1,5-pentanediol, 1,6-hexanediol, decamethylene glycol, cyclohexanediol, long chain glycols having molecular weights on the order of about 400—6,000 such as poly(ethylene glycol), poly(1,3-propylene glycol), poly(tetramethylene glycol) and the like. Mixtures of these glycols can also be employed.

Preferable polyesters are poly(ethylene terephthalate), poly(propylene terephthalate), poly(butylene terephthalate), poly(butylene sebacate), poly(ethylene 2,6-naphthalate), and copolyesters such as poly(ethylene isophthalate-terephthalate) (PETI), poly(butylene terephthalate-isophthalate) (PBTI) and the like. Among these poly(ethylene terephthalate) and poly(butylene terephthalate) are most preferably used because of their excellent mechanical properties.

Furthermore, mixtures as desired of the above polyesters and copolyesters may also be employed, and even a mixture of other organic polymer less than 30 parts by weight, with respect to 100 parts by weight of those polyesters can be applied to the present invention.

As the organic polymers employable in the above case, there may be mentioned polyethylenes, polypropylenes, ethylene-vinylacetate-copolymers, ethylene-acrylic ester-copolymers, ethylene-propylene-copolymers, butyl rubber, chlorinated polyethylenes, chlorinated polypropylenes, polybutadiene, polystyrene, styrene-acrylonitrile-butadiene resins, styrene-polyphenylene oxide resins, styrene-acrylonitrile copolymers, polyvinyl chlorides, polyoxymethylenes, polyamides, polyphenylene oxides, polytetrafluoroethylenes, ethylene tetrafluoroethylene copolymers polycarbonates etc.

The component (a) to be employed as the flame retarding agent in the present invention is the halogen containing polystyrene and/or halogen containing poly-α-methylstyrene represented by the general formula given earlier and may be produced by subjecting the halogenated styrene or halogenated-α-methylstyrene such as tribromostyrene to polymerization or by halogenating polystyrene or poly-α-methylstyrene.

The flame retarding agent of the general formula (I) can be used, even if other vinyl group compounds are copolymerized therewith. The vinyl group compounds in the above case include styrene, α-methylstyrene, acrylonitrile, methyl acrylate, butyl acrylate, methyl methacrylate, butadiene, vinyl acetate etc.

The amount of addition of halogen containing polystyrene and/or halogen containing poly-α-methyl styrene represented by the general formula (I) is 3 to 45 parts by weight and more preferably, 5 to 40 parts by weight with respect to 100 parts by weight of thermoplastic polyester, and if it is less than 3 parts by weight, sufficient flame retardancy is not obtained, while on the contrary, if it exceeds 45 parts by weight, the mechanical properties of the thermoplastic polyester are undesirably impaired.

The amount of addition of antimony trioxide is 1 to 20 parts by weight and more preferably, 3 to 18 parts by weight with respect to 100 parts by weight of thermoplastic polyester, and if it is less than 1 part by weight, the flame retardancy is not sufficient, while, if it exceeds 20 parts by weight, the mechanical properties of the thermoplastic polyester are undesirably impaired.

Still more preferably, it is desirable to add antimony trioxide at the rate of one antimony atom for every 2 to 5 halogen atoms in the added halogen containing polystyrene and/or halogen containing poly-α-methylstyrene. Simultaneously, other flame retarding assistants such as boron oxide, zirconium oxide, iron oxide. etc. may be employed.

The epoxy compound improves the mechanical properties such as impact resistance. etc., and also the thermal stability with simultaneous improvements of fluidity stabilization of the composition during molding in the fluid state.

As the epoxy compound which may be employed for the present invention, there may be mentioned, for example, tetrahydrophthalic acid diglycidyl ester, hexahydrophtalic acid diglycidyl ester, dimer acid diglycidyl ester, octadecanoic dicarboxylic acid diglycidyl ester, aliphatic acid monoglycidyl ester or ethylene/glycidyl methacrylate copolymer.

Particularly, undecanoic carboxylic acid monoglycidyl ester, tetrahydrophthalic acid diglycidyl ester, hexahydrophthalic acid diglycidyl ester and ethylene/glycidyl methacrylate copolymer may be favorably employed.

The amount of addition of these epoxy compounds should be in the range of 0.1 to 10 parts by weight and more preferably, 0.2 to 9 part by weight with respect to 100 parts by weight of the thermoplastic polyester, and if it is less than 0.1 part by weight, the improvement of mechanical properties, fluidity, etc., is small, while on the contrary, if it exceeds 10 parts by weight, the flame retardancy is undesirably impaired.

If desired, to the composition of the present invention may be added various additives such as fibrous or granular reinforcements and fibers including glass fibers, glass beads, carbon fibers, calcium carbonate, magnesium carbonates, barium sulfates, granular silicas, wollastonites, talcs, clays, micas, sericities, zeolites, bentonites, dolomites, kaolinites, asbestos, feldspars and the like; antioxidant and heat-stabilizers selected from hindered phenols, hydroquinones, thioethers, phosphites and the like; ultraviolet absorbent selected from various substituted benzotriazoles, benzophenones, salicylates, resorcinols and the like; lubricants and mold release agents selected from stearic acid, stearates, montanic acid, montan wax, montanates, stearyl alcohol, stearylamides such as ethylene bis(stearamide) and the like; coloring agent including dyes and pigments such as carbon black, titanium dioxide, cadmium sulfde and phthalocyanines: another flame retardants selected from halogen substituted aromatic compounds such as decarbromodiphenyl ether, brominated polycarbonates, melamine compounds, cyanuric acid derivatives, phosphorus compounds and the like; nucleating agents and antiwear agents and the like, as long as the characteristics of the resulting compositions are not adversely affected.

The composition of the present invention may be produced by the conventional methods, which include, for example, the process in which the thermoplastic polyester, halogen containing polystyrene and/or halogen containing poly-α-methylstyrene, antimony trioxide, epoxy compound and other necessary additives are subjected to melting and mixing in an extruder or kneader; the process in which, after uniformly mixing granular materials with each other mechanically, molding is effected simultaneously with mixing by a direct injection molding machine: and another process in which the additives are directly charged into a polymerizing vessel of resin for mixing, etc.

In the above case, although the addition may be effected in any order as desired, it is one of the preferable methods to mix the halogen containing polystyrene and/or halogen containing poly-α-methystyrene and antimony trioxide, after subjecting the thermoplastic polyester and epoxy compound to preliminary mixing.

The resinous composition of the present invention can be molded according to conventional methods such as extrusion molding, blow molding, injection molding and the like.

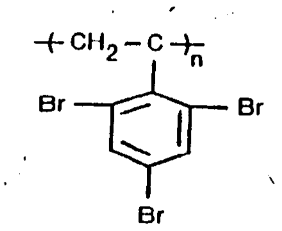
The molded products as described above are not only favorable in the flame retardancy, but also superior in fluidity and thermal stability, with a good surface appearance, and therefore, useful for mechanical components, electrical parts, and parts for motor vehicles, etc.

Hereinbelow, examples are inserted for the purpose of illustrating the present invention, without any intention of limiting the scope thereof.

It is to be noted that, in the examples to be given hereinbelow, % and parts are all based on weight, and that, in the illustrative examples and comparative examples, the properties of the resinous composition are determined according to the following methods:

Relative viscosity:	With o-chlorophenol employed as a solvent, polymer solution at 25% is measured at 25°C
Tensile property:	ASTM D—636
Flammability:	UL—94 (vertical burning test)
Thermal stability:	Tensile strength maintaining rate (%) after subjecting the molded products to dry heat treatment at 190°C for 15 days
Fluidity:	Filling minimum pressure (gauge pressure) during injection of the tensile molding piece is measured.

Example 1



35 parts by weight of glass fibers, 12 parts by weight of the flame retarding agent (A) as stated below, 5 parts by weight of antinomy trioxide, and 1 part by weight of barium stearate were mixed with 100 parts by weight of polyethylene terephthalate (PEET) with a relative viscosity of 1.35, with further addition thereto of various epoxy compounds as shown in Table 1 at the rate given in Table 1.

For the blending, the polyethylene terephthalate, flame retarding agent (A), antimony trioxide, barium stearate, and epoxy compounds were mixed by the V-blender, with subsequent addition thereto of the glass fibers.

The mixtures thus obtained were subjected to melting and kneading at 280°C with the use of the 65 mm ∅ extruder to be formed into pellets.

After subjecting these pellets to vacuum drying at 130°C for 5 hours, burning test pieces (0,32 × 1,27 × 12,7 cm and 0,08 × 1,27 × 12.7 cm) and tensile dumbbell test pieces were molded at a molding temperature of 280°C and a mold temperature of 130°C, and the minimum injection pressure at this time was recorded.

With the use of the above burning test pieces. the vertical burning test was effected according to UL—94 standard, while the tensile property test was made on the basis of ASTM D—638, the results of which are shown in Table 1.

Flame retarding agent (A)

TABLE 1

Epoxy compound (added amount)	Tensile properties		UL94 flammability 0,79 mm
	Tensile strength (kg/cm^2)	Elongation at break (%)	
EPIKOTE 815 ® (0.5) *) (bis-glycidylpolyether of bisphenol A)	1 380	3.6	V–0
EPIKOTE 190 ® (made by Shell Company) (Tetrahydrophthalic acid diglycidyl ester) (0.5)	1 490	4.1	V–0
CARDURA E ® (made by Shell Company) (Undecanoic carboxylic acid monoglycidyl ester) (0.5)	1 320	3.4	V–0
Ethylene glycidylmethacrylate copolymer (3.0)	1 510	3.6	V–0
None	1 190	3.2	V–0

*) comparison

From the results of Table 1, it is clear that the composition of the present invention is well balanced in the flammability and mechanical properties.

Example 2

15 parts by weight of the flame retarding agent (A) as employed in Example 1, 6 parts by weight of antimony

trioxide (SBO), 0.1 part by weight of di-stearylpentaerythritol diphosphite (trade name HI-MO® made by Sanko Kagaku) and 0.5 part by weight of EPIKOTE 190® were mixed with 100 parts by weight of polybutylene terephthalate having a relative viscosity at 1.48, and 35 parts by weight of glass fibers.

For the blending, polybutylene terephthalate pellets and flame retarding agent (A), antimony trioxide, di-stearyl-pentaerythritol diphosphite, and EPIKOTE 190® were first mixed by the V-blender preliminarily, and the glass fibers were mixed, with attention directed so as not to excessively open said glass fibers.

The resultant mixture was melted and kneaded at 250°C by the 66 mm ∅ extruder so as to be formed into pellets. The pellets thus obtained were formed after drying, into the burning test pieces (0,79 mm) and dumbbell test pieces at a molding temperature of 250°C and a mold temperature of 80°C.

Upon measurement of the flammability and tensile properties in the similar manner as in Example 1, the tensile strength of 1360 kg/cm^2 and UL94 flammability of V—O, were obtained, with the minimum injection pressure of 17 kg/cm^2 and thermal stability of 86%.

Meanwhile, as a result of similar tests made on the composition to which only EPIKOTE® was not added, the flammability was V—O, but the tensile strength was reduced to 1210 kg/cm^2, with simultaneous decrease of the minimum injection pressure to 9 kg/cm^2 and that of the thermal stability to 73%.

Example 3

100 parts by weight of polybutylene terephthalate with a relative viscosity of 1.70, 17 parts by weight of the flame retarding agent (A) employed in EXAMPLE 1, 7 parts by weight of antimony trioxide, 0.1 part by weight of thiodistearylpropionate (trade name Sumilizer TPS®, made by Sumitomo Kagaku), and 0.6 parts by weight of CARDURA E® as epoxy compound were mixed at the above rate.

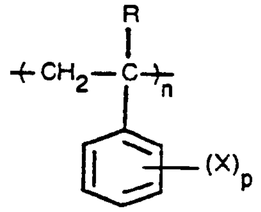
For the blending, the V-blender were employed, and the resultant mixture was melted and kneaded at 250°C with the use of a 30 mmo extruder to be formed into pellets. After having been dried in hot air at 130°C for 5 hours, the pellets were formed into the burning test pieces (3,17 mm) and dumbbell test pieces at a molding temperature of 250°C and a mold temperature of 80°C. Upon subjecting the test pieces to the tensile property tests and UL94 flammability tests in the similar manner as in Example 1, the tensile strength of 580 kg/cm^2, elongation at break of 40% and UL94 flammability of V—O were obtained.

When the physical property tests were made on the composition without addition of CARDURA E® in the similar manner, the flammability was still V—O, but the tensile strength was lowered to 560 kg/cm^2, with simultaneous reduction of the elongation at break to 20%.

Claims

1. A flame retarding polyester composition which comprises

(a) 3 to 45 parts by weight of a halogen containing polystyrene and/or a halogen containing poly-α-methyl-styrene represented by formula (I)



(I)

wherein R represents a hydrogen atom or methyl group, X represents a bromine or chlorine atom, p is an integer of 1 to 5, and n is an integer larger than 2,

(b) 1 to 20 parts by weight of antimony trioxide, and

(c) 0,1 to 10 parts by weight of an epoxy compound selected from the group consisting of glycidyl esters of aliphatic or cycloaliphatic carboxylic acids and ethylene-glycidyl methacrylate copolymer,

the amounts of (a), (b) and (c) being based upon 100 parts by weight of polyester in the polyester composition.

2. A flame retarding polyester composition as claimed in Claim 1, wherein said thermoplastic polyester is a polyethylene terephthalate.

3. A flame retarding polyester composition as claimed in Claim 1, wherein said thermoplastic polyester is a polybutylene terephthalate.

4. A flame retarding polyester composition as claimed in Claim 1, wherein said halogen containing polys-

tyrene is a polytribromostyrene.

5. A flame retarding polyester composition as claimed in Claim 1 or 4, wherein the total amount of halogen containing polystyrene and/or halogen containing poly-α-methylstyrene is in the range of 5 to 40 parts by weight.

6. A flame retarding polyester composition as claimed in Claim 1, wherein the amount of addition of the epoxy compound is in the range of 0.2 to 9 parts by weight.

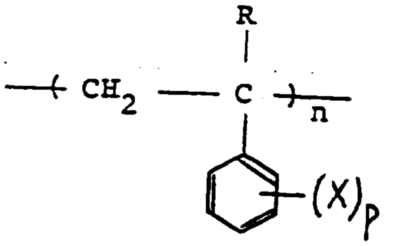
7. A flame retarding polyester composition as claimed in Claim 1, further containing fibrous and/or granular reinforcement.

8. A flame retarding polyester composition as claimed in Claim 7, wherein said reinforcement is glass fibers.

Revendications

1. Composition de polyester ignifuge qui comprend :

(a) 3 à 45 parties en poids d'un polystyrène contenant des halogènes et/ou d'un poly-α-methylstyrène contenant des halogènes représentés par la formule (I)



(I)

où R représente un atome d'hydrogène ou le groupe méthyle, X représente un atome de chlore ou de brome, p est un nombre entier de 1 à 5 et n est un nombre entier supérieur à 2

(b) 1 à 20 parties en poids de trioxyde d'antimoine, et

(c) 0,1 à 10 parties en poids d'un composé époxy choisi dans le groupe se composant d'esters glycidyliques d'acides aliphatiques ou cycloaliphatiques carboxyliques, et de copolymère éthylène-méthacrylate de glycidyle,

les quantités de (a), de (b) et de (c) étant basées sur 100 parties en poids de polyester dans la composition de polyester.

2. Composition de polyester ignifuge selon la revendication 1, dans laquelle le polyester thermoplastique est un téréphtalate de polyéthylène.

3. Composition de polyester ignifuge selon la revendication 1, dans laquelle le polyester thermoplastique est un térephtalate de polybutylène.

4. Composition de polyester ignifuge selon la revendication 1,dans laquelle le polystyrène contenant des halogènes est un polytribromostyrène.

5. Composition de polyester ignifuge selon la revendication 1 ou 4, dans laquelle la quantité totale de polystyrène contenant des halogènes et/ou du poly-α-méthylstyrène contenant des halogènes est dans la gamme de 5 à 40 parties en poids.

6. Composition de polyester ignifuge selon la revendication 1, dans laquelle la quantité d'addition du composé époxy est dans La gamme de 0,2 à 9 parties en poids.

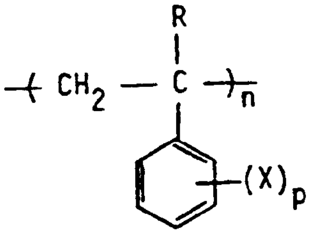
7. Composition de polyester ignifuge selon la revendication 1, contenant en outre un renforcement fibreux et/ou granulaire.

8. Composition de polyester ignifuge selon la revendication 7, dans laquelle le renforcement est constitué de fibres de verre.

Patentansprüche

1. Flammhemmende Polyester-Zusammensetzung, die umfaßt

(a) 3 bis 45 Gewichtsteile eines halogenhaltigen Polystyrols und/oder eines halogenhaltigen Poly-α-methylstyrols gemäß der Formel (I)



$$-\!\!\left(CH_2-\overset{R}{\underset{C_6H_{5-p}(X)_p}{C}}\right)_n-$$

(I)

in der R ein Wasserstoffatom oder eine Methylgruppe bedeutet, X ein Brom- oder Chlor-Atom bedeutet, p eine ganze Zahl von 1 bis 5 ist und n eine ganze Zahl größer als 2 ist,

(b) 1 bis 20 Gewichtsteile Antimontrioxid, und

(c) 0,1 bis 10 Gewichtsteile einer Epoxid-Verbindung, die aus der Gruppe ausgewählt ist, die aus Glycidylestern von aliphatischen oder cycloaliphatischen Carbonsäuren

und einem Ethylen-Glycidylmethacrylat-Copolymeren besteht, wobei die Mengen von (a), (b) und (c) auf 100 Gewichtsteile Polyester in der Polyesterzusammensetzung bezogen sind.

2. Flammhemmende Polyester-Zusammensetzung nach Anspruch 1, bei der der genannte thermoplastische Polyester ein Polyethylenterephthalat ist.

3. Flammhemmende Polyester-Zusammensetzung nach Anspruch 1, bei der der genannte thermoplastische Polyester ein Polybutylenterephthalat ist.

4. Flammhemmende Polyester-Zusammensetzung nach Anspruch 1, bei der das genannte halogenhaltige Polystyrol ein Polytribromstyrol ist.

5. Flammhemmende Polyester-Zusammensetzung nach Anspruch 1 oder 4, bei der die Gesamtmenge an halogenhaltigem Polystyrol und/oder halogenhaltigem Poly-α-methylstyrol im Bereich von 5 bis 40 Gewichtsteilen liegt.

6. Flammhemmende Polyester-Zusammensetzung nach Anspruch 1, bei der die Zugabemenge der Epoxid-Verbindung im Bereich von 0,2 bis 9 Gewichtsteilen liegt.

7. Flammhemmende Polyester-Zusammensetzung nach Anspruch 1, die außerdem eine faserige und/oder körnige Verstärkung enthält.

8. Flammhemmende Polyester-Zusammensetzung nach Anspruch 7, bei der die genannte Verstärkung Glasfasern sind.